PBDEs IN LANDFILL LEACHATE AND POTENTIAL FOR TRANSFER FROM ELECTRONIC WASTE

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Introduction

Polybrominated diphenyl ethers (PBDEs) have the potential to be persistent, toxic and prone to long-range transport in the environment[1]. Research on brominated flame retardants (BFRs), including PBDEs, has largely focused on environmental concentrations and potential for adverse health and ecological effects. An important question deserving greater attention is how PBDEs are transferred from waste streams to air, water and soil, and how they are transported to distant locations such as the Arctic region. One likely source is from landfills, which receive a large proportion of society's discarded consumer waste products includingelectronic equipment, furniture, and other flame-retarded household and industrial products. PBDEs are chemically synthesized and have been known to constitute up to 30% of such final products as computers, television sets, and upholstery. Concerns have been raised that PBDEs may disrupt endocrine function and have the potential to surpass PCB concentrations in the environment[2]. Some BFRs are persistent in the environment.

Although leaching of compounds from plastics in the short term is generally low, several studies have measured plasticizers, phthalates, and other organic chemicals in plastic waste over time[3]. In most manufacturing processes, PBDEs are embedded in plastic at the moulding stage. There is little available information, to date, on whether PBDEs behave similar to that observed for other plastic additives in landfilled electronic waste. For example, neither the rate at which PBDEs are released from plastic nor their potential for degradation in leachate is known. Therefore, long-term diffuse emissions from landfills are a possibility that must be considered[4,5].

This paper reports preliminary results of on-going research examining municipal landfills as a source of PBDEs in Canada. PBDE concentrations were determined in leachates collected from individual waste disposal cells at a municipal landfill that receives a broad range of waste, currently operating in British Columbia. Using available waste disposal records, each disposal cell could be associated with a specific period of operation, thereby providing the opportunity to examine not only PBDE composition in the leachate from each cell, but also a temporal picture of how PBDE levels relate to society's waste over the past 3 decades (1980 to 2005). A related study examined the potential for PBDE leaching from electronic waste (e-waste) representing different disposal periods. Landfill leachates and distilled water were contacted with crushed e-waste materials, comprised predominantly of computer casings, hard drives, keyboards, mice, printers and scanners, and tested for their PBDE concentrations at different time intervals.

Methods

Leachate was collected from different disposal cells dedicated to handling waste during five time periods: 1980-1984, 1985-1989, 1990-1994, 1995-1999 and 2000-2005. Leachate collection systems are isolated in each disposal cell. Leachate was collected by manually pumping from the water table using Waterra® tubing with a foot valve fitted at the bottom to dark amber glass bottles. Samples were stored at 4°C until analysis. Waste electric and electronic equipment items representing each 5-yr period were provided by Genesis Recycling Ltd. (Aldergrove, BC, Canada). Metal components were removed and the remaining plastic waste ground in a shredding chamber to pieces of approximately 2 mm volume-equivalent diameter.

Leaching tests in the laboratory were performed using 100 g of shredded waste sonicated in distilled water for 2 h to remove the dust-sized particles. Leachate from the landfill or distilled water were then combined in sealed stainless steel columns and mixed in an end-over-end contacting chamber at 8 rpm at atmospheric pressure and room temperature (~20°C) for predetermined mixing periods. Leachate was decanted into 1 L flasks, double filtered to remove particulates, and stored at 4°C prior to analysis.

Before analyzing for PBDE congeners, leachate collected either directly from the landfill or after mixing with e-wastes in laboratory leaching tests was centrifuged at 2300-2500 x g for 10 min. to separate the aqueous and solid phases. The distilled water fractions and e-waste were filtered and the aqueous portion extracted 3 times with tmethylene chloride. The solid portion was discarded. PBDE homologue and congener-specific analyses were carried out at the Institute of Ocean Sciences, Department of Fisheries and Oceans Canada (Sidney, BC, Canada) and at Alta Analytical Laboratory (El Dorado Hills, CA USA) using high-resolution gas chromatography/mass spectrometry methods described elsewhere[6,7,8].

Results and Discussion

PBDE concentrations in landfill leachate and e-waste from disposal cells operating for 5-yr periods between 1980 and 2005 are summarized in Table 1. Results from pre-1980s may represent PBDE levels prior to widespread usage, which began in the 1980s. PBDE concentrations increase in leachate from the early and late 1980s, decrease in the early 1990s, then show marked increases after 1995. Leachate collected from a disposal cell operating during 2000-2005 was 2-orders of magnitude higher in penta-BDE and other congeners than leachate representing pre-1980s e-waste disposal (Table 1). PBDE levels in leachate correlated closely with levels in shredded solid e-waste. PBDE concentrations in e-waste from 1985-1989 were 3-6 order of magnitude higher than in subsequent years, which may reflect either a higher usage of PBDEs during the 1980s than other decades or different methods of incorporating these compounds into plastics. PBDE levels were markedly lower by the late 1990s, and no Deca-BDE was detectable in e-waste from 2000-2005.

In general, the results shown in Table 2 suggest that PBDE levels may have the potential to increase further in landfill leachate, based on results of laboratory leaching tests conducted to extract PBDEs from shredded e-waste. For example, PBDE concentrations in landfill leachate mixed with e-waste from 1985-1989 increased by 7 times for both tetra-BDEs and hexa-BDEs; penta-BDE and hepta-BDE levels increased by 2.5 and 40 times, respectively. Even higher increases were observed in landfill leachate mixed with e-waste from 1990-1994; PBDE levels increased 3.5-, 660- and 3,000- fold for penta-, hexa- and hepta-BDEs, respectively. Similar increases were evident using e-waste from 1995-1999. In contrast, PBDE levels only slightly increased in landfill leachate mixed with e-waste from 2000-2005, with the exception of hepta-BDE (which increased 75-fold).

As expected, the results of mixing distilled water with e-waste representing each decade of disposal for 1, 24 and 168 h in the end-over-end contacting chamber at 8 rpm differed considerably from those using landfill leachate at pH 7 (Figures 1 and 2). There was little or no transfer of PBDEs to the liquid phase from e-waste originating after 2000, perhaps due to the low solubility of PBDEs in distilled water. In contrast, however, there was significant transfer of PBDEs from e-waste representing the 1980s, possibly due to detergents or other surfactants associated with the e-wastes; although, there was no clear trend with the duration of contacting.

Conclusions

These preliminary results indicate the potential for significant transfer of PBDEs from e-wastes to landfill leachate, demonstrating the importance of landfill leachate collection systems for minimizing release of these contaminants into the environment. Significant differences in PBDE levels in leachate corresponding to different 5-yr periods suggest that the time-of-manufacture of electronic goods may well be an important factor in determining the rate of PBDE release to the environment. The highest levels occur in leachate corresponding to the 1985-1989 period. The data generally show a reduction in PBDE congener concentrations with the passage of time. This may be due either to changes in the use of PBDEs in products over the past 3 decades or to other factors such as

decomposition and/or preferential transfer. The leachate itself may also be factor, since decreasing pH led to a significant increase in the transfer of PBDEs from crushed e-waste to leachate. These preliminary results, together with on-going work, will be used to develop a mass balance model to predict the environmental fate of PBDEs from electronic waste streams in Canada[9,10].

Acknowledgements

We gratefully acknowledge Environment Canada, Department of Fisheries and Oceans Canada, Alta Analytical Laboratory, Genesis Recycling Ltd., and ENVIRON for their support of this research.

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Table 1. PBDEs in electronic-waste (e-waste; pg/g) and leachate (pg/L) collected from landfill cells representing 1980-2005 (Source: Alta Analytical Lab)

(Congeners - totals/group)	e-waste	leachate	e-waste	leachate	e-waste	leachate	e-waste	leachate	e-waste	leachate
	1980-1984		1985-1989		1990-1994		1995-1999		2000-2005	
MonoBDEs	ND	157	52,200	119	ND	134	ND	243	ND	317
DiBDEs	382	27.2	119,000	45	304	27.5	44	352	91	639
TriBDEs	259	77.9	253,000	37	220	87.9	80	977	89	6,490
TetraBDEs	5,910	332	1,110,000	522	1,290	393	3,030	15,300	1,550	355,000
PentaBDEs	14,000	394	36,100,000	644	1,760	343	5,900	35,700	2,690	743,000
HexaBDEs	387,000	0	1,530,000,000	855	2,710	390	8,780	13,800	1,710	257,000
HeptaBDEs	1,670,000	1,220	2,050,000,000	2,190	19,800	907	26,700	4,650	5,040	20,400
OctaBDEs	1,540,000	548	5,190,000,000	3,450	18,000	1,450	19,600	4,050	3,210	17,800
NonaBDEs	801,000	0	1,910,000,000	2,280	40,600	966	ND	2,550	ND	11,500
DecaBDEs	7,530,000	0	1,670,000,000	5,300	268,000	2,710	41,200	10,000	ND	56,700
Total BDEs	11,948,551	2,756	12,387,634,200	15,442	352,684	7,408	105,334	87,622	14,380	1,468,846

Table 2. Leachate + e-waste 1985-2005 after 1 h contact time (Source: DFO)

Year	**1985-1989**	**1990-1994**	**1995-1999**	**2000-2005**
BDE Congeners				
Total Mono-BDE	0	0	0	0
Total Di-BDE	0	560	0	480
Total Tri-BDE	3,030	720	1,590	5,880
Total Tetra-BDE	224,130	8,640	138,820	404,200
Total Penta-BDE	80,910	15,540	378,080	834,830
Total Hexa-BDE	88,880	666,620	201,210	580,780
Total Hepta-BDE	373,300	2,934,130	537,810	1,890,800

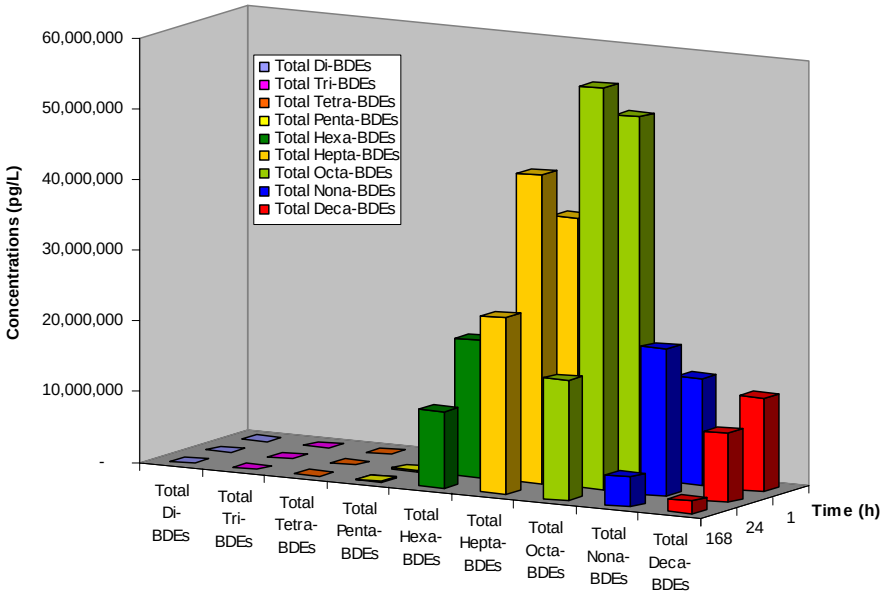

Figure 1. PBDE concentrations in distilled water mixed for 1, 24 and 168 h with e-waste representing the 1980s disposal period

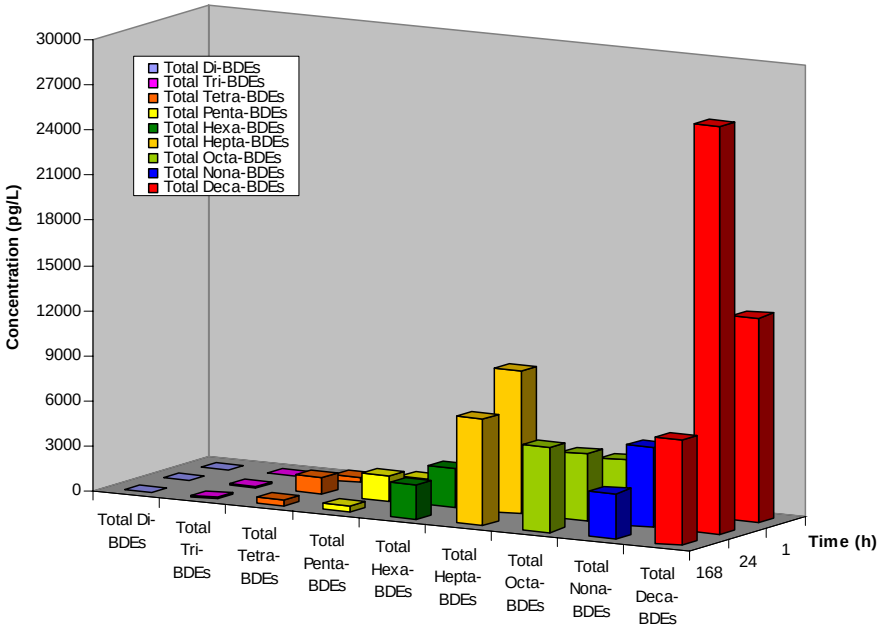

Figure 2. PBDE concentrations in distilled water mixed for 1, 24 and 168 h with e-waste representing the 2000s disposal period